

Characterization and Breakdown of South Gabal EL A'urf Polyminerized ore Material

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Abstract

The polyminerized ore material of south Gabal EL A'urf area hosts several economic minerals. These include tautouxenite, monazite, bastanasite, anatase, as well as zircon. The corresponding interesting rare metals of these minerals include Nb, Ta, lanthanides (REE), Ti, and Zr.

Different breakdown techniques have been investigated namely; agitation, pug and fusion. The latter technique is found to be preferred under the following conditions; potassium bisulphate ore/reagent weight ratio of 1/3 at 650 °C for 3h. The realized dissolution efficiencies for all metal values were as follows 98.0% and 99.3% for Nb and Ta respectively as well as complete dissolution for lanthanides (REE) and 94% for Ti while Zr did not exceed 20% and concentrated in the residue left behind.

This study of breakdown techniques aims to characterization of ore material of south Gabal EL A'urf area as well as preparing a proper leach liquor suitable for further recovery procedure and obtain pure remarkable products.

Introduction

A polyminerized ore material has been lately reported in south Gabal EL A'urf area, central Eastern Desert, Egypt [1]. This mineralization includes tautouxenite, monazite, bastanasite, anatase and zircon. The corresponding interesting rare metals of these minerals include Nb, Ta, REE, Ti, and Zr. The present work has been oriented towards the characterization of this mineralization mineralogically and chemically. For this purpose, a technological sample was properly collected and first subjected to mineralogical study to identify its mineral constituents as well as possible separation of certain mineral in certain size fraction, then applying different breakdown techniques for preparing a proper leach liquor suitable for further separation and recovery procedure.

Several studies have been applied on such ore material; Shaw and Lindstrom [2] recovered the metal values of the euxenite mineral by fusion with $(\text{NH}_4)_2\text{SO}_4$ or $(\text{NH}_4)\text{HSO}_4$ at 400 °C for 4 hours.

Shaw [3] indicated that euxenite from Arizona is amenable to REE recovery by digestion with HF- H_2SO_4 acid mixture. Shaw and Bauer (4) treated Idaho euxenite by H_2SO_4 acid alone for REE recovery. Pittuck et al [5] performed caustic fusion process for euxenite and fergusonite that assayed 9.4% U_3O_8 and 12.4% Nb_2O_5 at 700 °C for 10-15 min with S/R ratio 1/3.

El Hazek [6] studied the recovery of valuable metals from polyminerized ore material containing samarskite, betafite, thorite, uranophane and zircon. The ore concentrate assayed 31.77% RE_2O_3 , 20.78% Nb_2O_5 , 9.09% ZrO_2 , 6.45% ThO_2 , 2.2% U_3O_8 and only 1.06% Ta_2O_5 as well as 0.33% TiO_2 . This ore material subjected to H_2SO_4 agitation leaching to dissolve U, Th and REE while keeping Nb, Ta, Ti and Zr in the residue for subsequent leaching by HF. Moreover, El Hussaini and Mahdy [7] have been studied the recovery of different metals from ore material containing fergusonite and euxenite beside the refractory U mineral davidite. Using agitation $\text{H}_2\text{SO}_4/\text{HNO}_3$ acid mixture, almost complete leaching of Nb and Ta was obtained together with 86% of Th and 70% of the REE, however, U and Ti leaching efficiencies did not exceed 60%.

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Experimental

Ore Characterization

Mineralogical composition of south Gabal El-A'urf ore material

To identify the economic mineral constituents of south Gabal El-A'urf ore material, a representative bulk heavy fraction (bromofrom) was examined by X-ray diffraction technique (XRD). Using Philips x-ray diffractometer, model PW 223/20 in which the copper tube was operated at 49 Kv and 20 mA. Possible physical upgrading of certain mineral in certain size fraction was investigated where each of the obtained size fractions was ground to -200 mesh, attacked by a mixture of acids and analyzed for the interesting metals.

Chemical composition of south Gabal El-A'urf ore material

The representative sample of the studied south Gabal El-A'urf ore material was first ground to -200 mesh grain size and analyzed for its major and trace elements constituents using aqua regia and acids mixture. In the meantime, a total loss of ignition obtained at 1000 °C. This loss corresponding to humidity, combined water, CO₂ as well as possible organic matter.

Ore Breakdown (Leaching) Procedures

The ore sample was ground to pass -200 mesh sizes (65µm) and mixed well. After quartering, several representative sample portions were taken for study leaching experiments where three ore breakdown techniques have been applied namely; sulfuric acid agitation leaching, sulfatizing roasting (pug leaching) and potassium bisulfate fusion.

H₂SO₄ acid agitation leaching

Each leaching experiment has been performed by agitating a weighed amount of the ground sample with the acid of different concentrations with different solid/liquid ratios for different time periods at different temperature degrees. In these experiments, a hot plate with magnetic stirrer were used and precautions were taken for avoid evaporation. The obtained slurry then cooled, filtered, washed with distilled water and made up to volume. The residue left behind was subsequently dissolved in concent-

rated HF, filtered, washed with distilled water and made up to volume, then both solutions analyzed to calculate the dissolution efficiency percent according to the equation:

$$\% \text{ Leaching efficiency} = \frac{\text{Metal concentration in the leach liquor}}{\text{Original metal concentration in the ore}} \times 100$$

Sulfatizing roasting (pug leaching)

Sulfatizing roasting experiments were applied using conc. H₂SO₄ where a weighed portion from the finely ground sample mixed well with a proper amount of conc. acid in glass watches and allowed for roasting at different temperature degrees in a muffle furnace for certain time. The obtained paste was then cooled and agitated with 2N H₂SO₄ in a S/L ratio of 1 : 2.5 for 3 hrs at 300 °C. After cooling, the slurry was filtered, washed with distilled water, made up to volume for analyzing the dissolved metal values and calculate the dissolution efficiency.

Bisulfate fusion

Several fusion experiments have been performed using KHSO₄. In these experiments, different amounts of KHSO₄ were mixed with sample portions in a porcelain crucibles for different time periods and different temperature degrees. The obtained melt was then cooled and washed with distilled water, filtered and made up to volume for analyzing the interesting metal values and calculate the dissolution efficiency percent.

Analytical Procedures

Determination of the interesting metal values whether in the original sample or during processing streams will be summarized as follows: Ti, Nb, Ta and Zr were analyzed by the atomic absorption technique using a Unicam model 969 (Nitrous-Air acetylene flame), auto gas box at the wavelengths 365.4 nm 334.4 nm, 271.5nm and 360.1nm respectively. (Weltz and Sperling 1999) [8]. A spectrophotometric method using a double-beam UV-Visible Shimadzu (model 160A) was applied for REE where they form stable colored complex with Arsenazo III in weakly acidic media at pH about 2.6 and the absorbance measured at wavelength 650 nm against a reagent blank solution (Marczenko,1986) [9]. Ca and Mg were determined by a titrimetric method using EDTA. Na and K were determined by flame photometry.

Results and Discussion

Ore Characterization

Mineralogical composition of south Gabal El-A'urf ore material

To identify the economic mineral constituents of south Gabal El-A'urf ore material, a representative bulk heavy fraction (bromoform) was examined by XRD. From the obtained data, it was found that the principal minerals involve ASTM [10] tautouxenite 8-293, monazite 11-556, bastanasite 11-340, anatase

21-1272, and zircon 6-0266. In other words, it can be mentioned that Nb, Ta and some of REEs are found in tautouxenite mineral while the rest of REEs are found in both bastanasite and monazite. Ti is found as anatase while Zr is found as Zircon.

Possible physical upgrading of certain mineral in certain size fraction was investigated by sieving a representative portion of the ore material with a set of sieves ranging from 500 μm down to 100 μm (+35 to -140 mesh size), each of the obtained size fractions was ground to -200 mesh, attacked by acids mixture and analyzed for the interesting metals. The obtained data are tabulated in Table (1).

Table 1.
Metal concentration in fractions of south Gabal El-A'urf ore material

Grain Size		Concentration of Metals, %				
μm	Mesh	Nb	Ta	REEs	Ti	Zr
+500	+35	16.22	13.45	13.30	20.00	14.30
-500 +400	-35 + 40	18.00	21.90	17.30	17.50	22.70
-400 +300	-40 + 45	21.74	21.20	26.60	18.20	21.75
-300 +200	-45 + 70	22.74	20.90	20.10	16.30	20.00
-200 +100	-70 +140	21.30	22.55	22.70	28.00	21.20

From the obtained data, it is clear that no preferential concentration of any of the interesting metals in certain size fraction since their assay is almost comparable in.

Chemical composition of south Gabal El-A'urf ore material

Chemical composition of south Gabal El-A'urf ore material shown in Table (2) showed that the ore material is mainly composed of SiO_2 beside Al_2O_3 and Fe_2O_3 that attained 5% and 5.1% respectively as well as high K_2O content (4.92%). In the meantime, a total loss of ignition of about 0.74 was obtained at 1000°C. This loss corresponding to humidity, combined water, CO_2 as well as possible organic matter. On the other hand, analysis of the economic trace metals involved RE_2O_3 1.9%, Nb_2O_5 1.25% as well as TiO_2 and ZrO_2 1.23% and 1.12% respectively beside Ta_2O_5 0.13%.

Table 2.
Chemical composition of south Gabal El-A'urf ore material

Major constituent	Wt., %	trace constituent	Wt., %
SiO_2	74.00	RE_2O_3	1.90
TiO_2	1.23	Nb_2O_5	1.25
Al_2O_3	5.00	Ta_2O_5	0.13
Fe_2O_3	5.10	ZrO_2	1.12
CaO	1.64	U_3O_8	0.01
MgO	0.80	ThO_2	0.04
MnO	0.05		
Na_2O	2.13		
K_2O	4.92		
P_2O_5	0.06		
L.O.I	0.74		
Total			100.12

Ore Breakdown Techniques

H_2SO_4 acid agitation leaching

i- Effect of H_2SO_4 acid concentration

A set of leaching experiments have been performed using different concentrations of H_2SO_4 acid ranging from 200 to 1800 g/l. The other leaching conditions were fixed at 300 °C for 3h with S/L ratio of 1/3. The obtained leaching efficiencies plotted in Fig. (1) showed that REE and Ti increased from 55.7

to 81.0 % and from 62.2 to 84.8 % respectively by increasing the acid conc. from 200 to 800 g/l. Further increase in acid concentration keeps comparable results for REE and Ti leaching efficiencies.

However, Zr leaching efficiency didn't exceed 10.55 % as it requires higher temp. more than 300 °C. On the other hand, Nb and Ta bad dissolution necessitates the presence of HF acid or much sever conditions to breakdown the mineral lattice and facilitate their dissolution.

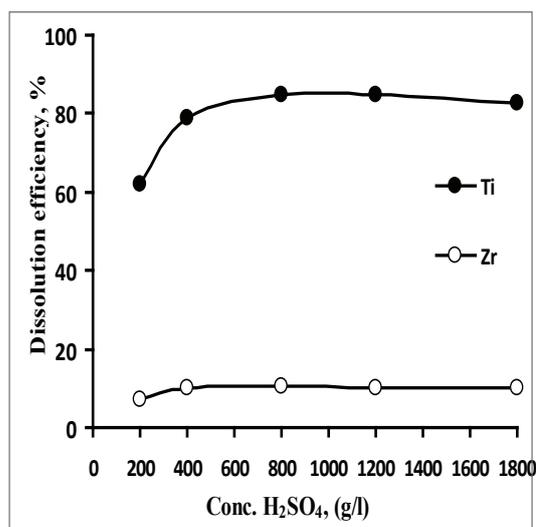
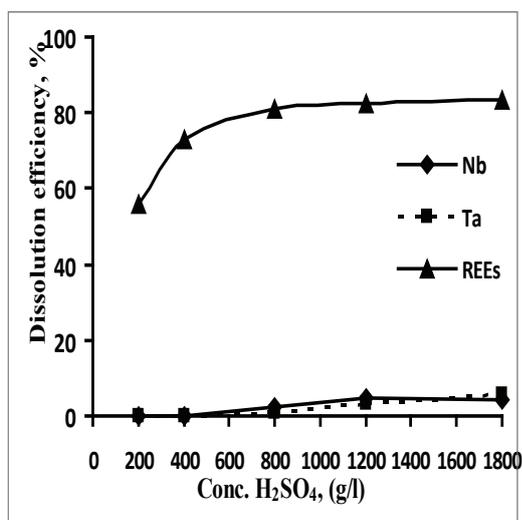


Fig. 1. Effect of H_2SO_4 conc. upon dissolution of the metals of south Gabal El-A'urf ore material.

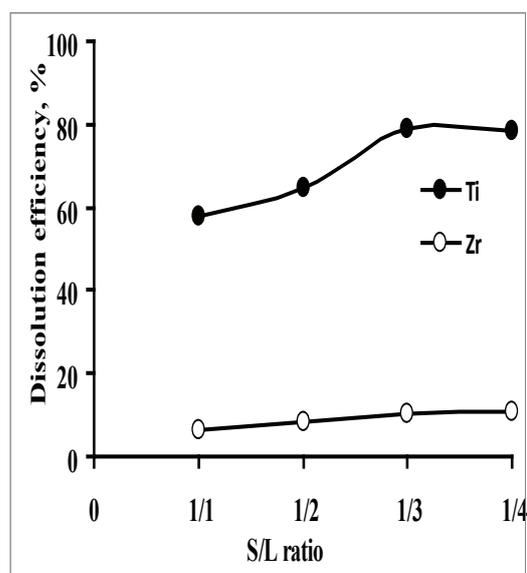
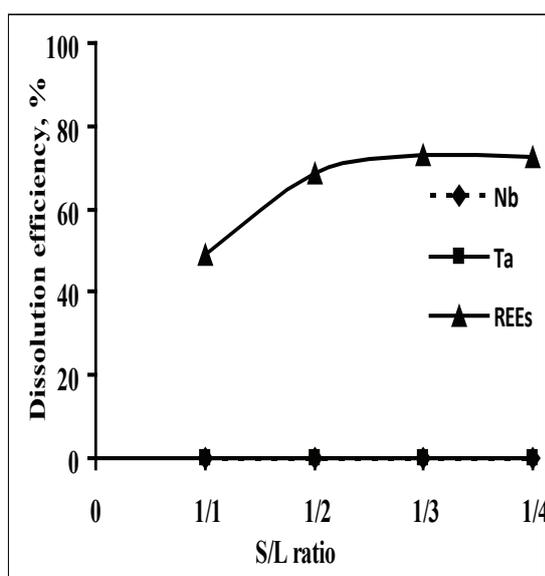


Fig. 2. Effect of S/L ratio upon dissolution of the metals of south Gabal El-A'urf ore material.

ii- Effect of solid/liquid ratio (S/L)

The effect of S/L ratio (ore/ H₂SO₄ acid ratio) upon the dissolution of the interesting metals was studied with S/L ratios ranging from 1/1 to 1/5 using 400 g/l H₂SO₄ acid at 300°C for 3h. Leaching efficiencies plotted on Fig.(2) indicated that 400 g/l H₂SO₄ cannot breakdown the Nb-Ta mineral lattice even at 1/4 S/L ratio. In the meantime, REE and Ti dissolution efficiencies increased to 73.00 % and 78.9 % at 1/3 S/L ratio and almost kept steady at S/L ratio of 1/4.

iii- Effect of leaching temperature

The effect of leaching temp. has been investigated at temperature degrees ranging from 150 up to 350 °C under other fixed conditions of 400 g/l H₂SO₄ conc., S/L ratio of 1/3 and leaching time 3h. The data obtained illustrated on Fig.(3) indicated that the refractory nature of the poly-mineralized ore material has required high temp. up to 350 °C to be broken. So the ore breakdown requires either higher temp. than 350°C or using HF acid to facilitate the minerals breakdown. However, partial separation of Nb, Ta & Zr from REE and Ti could be achieved at 300 °C.

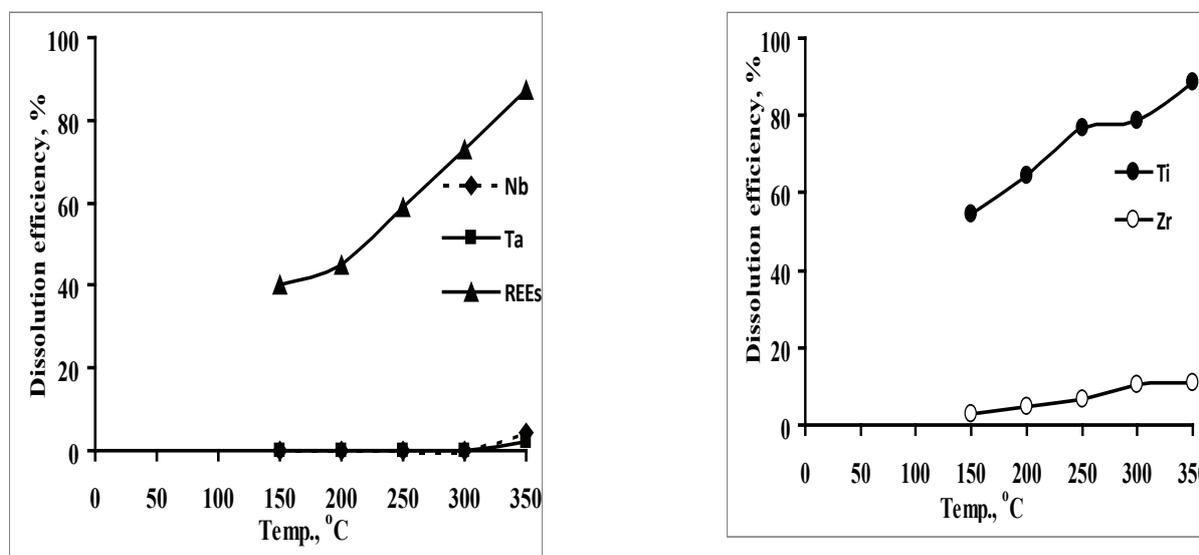


Fig. 3. Effect of leaching temp. upon dissolution of the metals of south Gabal El-A>urf ore material.

iv- Effect of leaching time

A set of leaching experiments has been performed at different times ranging from 1 to 4 h. The other leaching conditions fixed at H₂SO₄ conc. of 400 g/l, 1/3 S/L ratio at 300 °C. The corresponding leaching efficiencies plotted in Fig. (4) indicated that the polymineralized ore material required long leaching periods, where REE and Ti leaching efficiencies were 45.1 % and 53.0 % at 1 h. Extending leaching time up to 3 and 4 h increased the leaching efficiencies of REE to 73.8 and 79.8 % respectively while Ti increased to 78.8%. Noticed that Nb and Ta leaching efficiencies began to appear at 4 h.

v- Effect of HF acid addition

A series of leaching experiments has been performed with HF addition (to H₂SO₄) with S/L ratios ranging from 1/1 to 1/5 of the ore weight to improve

Nb & Ta dissolution efficiencies. The other fixed leaching conditions were 400 g/l H₂SO₄ conc., S/L ratio of 1/3 at 300 °C for 3 h. The corresponding leaching efficiencies plotted in Fig. (5) showed the importance of HF acid addition to bring out almost complete dissolution of Nb and Ta where they attained 95.00 % and 94.00 % respectively at S/L ratio of 1/5 but with partial precipitation for REE and Ti while keeping Zr not affected.

Finally, from the foregoing agitation leaching study, it can be concluded that this technique is not efficient in dissolving most of the interesting metals from south Gabal El-A>urf polymineralized ore material. Otherwise, the sulfate leach liquor should be separated before the HF addition to keep REE and Ti contents, also to dissolve Nb and Ta in separate HF leach liquor.

The best agitation experimental conditions:

- Acid concentration : 400 g/l H₂SO₄, 40% HF
- S/L ratio : 1/3 H₂SO₄, 1/5 HF
- Temperature : 300 °C
- Time : 3 h

Pug acid leaching

i-Effect of H₂SO₄ amount (volume)

A series of experiments has been performed by

mixing ore portions with different volumes of conc. H₂SO₄; 5, 10, 15, 20 and 25 ml. The curing temperature was fixed at 350 °C for 6 h. The results plotted on Fig. (6) indicated that the maximum leaching efficiencies of Nb, Ta, REE, Ti & Zr did not exceed 30.1, 26.7, 76, 89 & 11.6 % respectively using 10 ml H₂SO₄. Increasing the acid amount, decreases the leaching efficiencies of the metal values. This may be due to dissolution of Fe (Fernaz) [11] and/or other impurities which would increase using concentrated acid (Terry) [12].

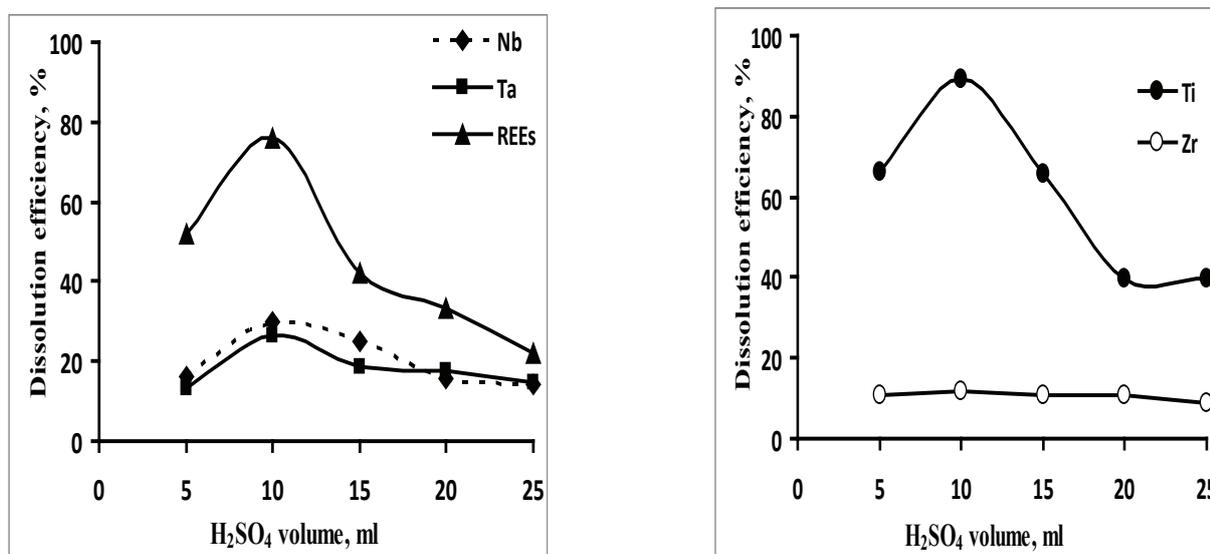


Fig. 6. Effect of H₂SO₄ amount (volume) upon dissolution of the metals of south Gabal El-A'urf ore material.

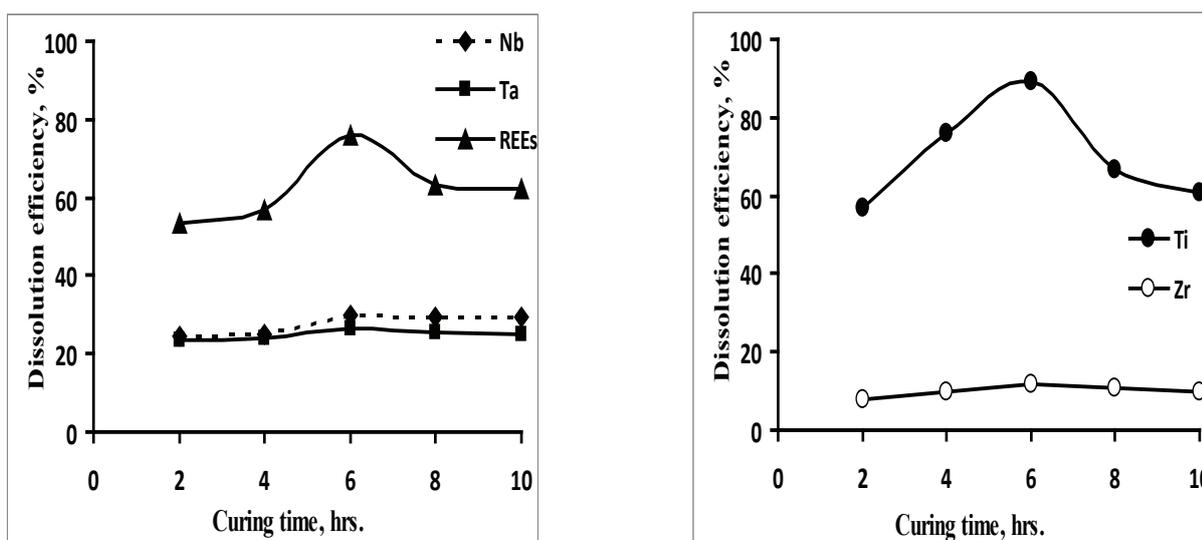
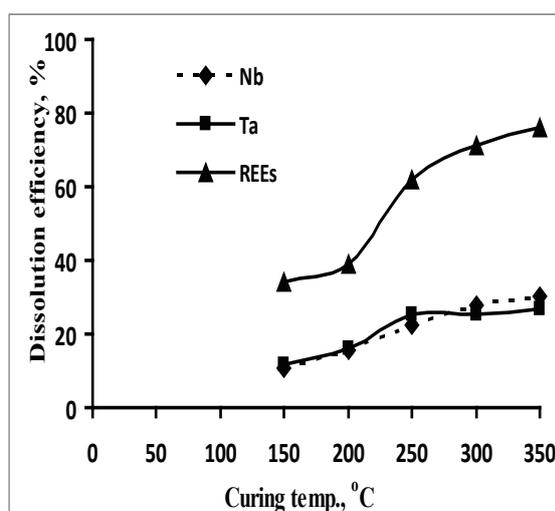


Fig. 7. Effect of curing time upon dissolution of the metals of south Gabal El-A'urf ore material.

ii- Effect of curing time

A set of leaching experiments has been performed at different time periods ranging from 2 to 10 h. The other leaching conditions were fixed at H_2SO_4 amount of 10 ml at 350 °C. The obtained results plotted on Fig. (7) showed that the dissolution efficiencies of all interesting metal values increased by increasing curing time till 6 h. where Nb attained 30.1 %, Ta 26.7 %, Ti 89 %, REE 76.00 % and Zr 11.6 %. After 6 h, the dissolution efficiencies of all metal values began to decrease most probably due to hydrolysis.



iii-Effect of curing temperature

A series of pug leaching experiments has been applied using different curing temp. degrees ranging from 150 to 350 °C. The other leaching factors were fixed at acid volume of 10ml for of 6 h curing time. The results plotted on Fig. (8) proved increasing the dissolution efficiencies by increasing temp. to 350 °C for all metals where Nb attained 30.1%, Ta 26.7 %, REE 76 %, Ti 89 % and Zr 11.6 %.

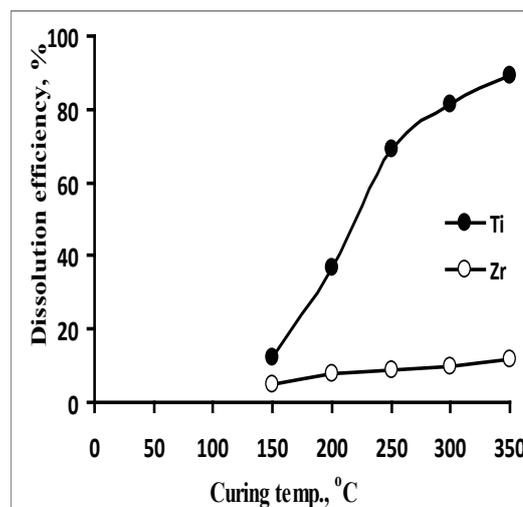


Fig. 8. Effect of curing temp. upon dissolution of the metals of south Gabal El-A>urf ore material.

From the foregoing pug leaching study, it can be stated that the best pug leaching conditions were H_2SO_4 amount of 10 ml at 350 °C for 6 h. This resulted in 30.1 %, 26.7 %, 76 % & 89 % as leaching efficiencies for Nb, Ta, REE & Ti respectively while Zr not exceed 11.6 %.

Fusion

i- Effect of ore / $KHSO_4$ ratio (S/R)

A set of experiments has been performed using different S/R (ore/ $KHSO_4$) ratios ranging from 1:1 to 1:4 while the other fusion conditions were fixed at 650 °C for 3 h. The results plotted on Fig. (9) proved that the dissolution efficiencies of the interesting metals increased at 1/3 ore / $KHSO_4$ ratio where almost complete dissolution for Nb, Ta & REE and reached about 94 & 20% for Ti & Zr respectively. Using 1/4

S/R ratio decreases the leaching efficiencies for all metals except Zr most probably due to hydrolysis.

ii- Effect of fusion temperature

A series of experiments has been studied at temp. ranging from 350 to 750 °C. Other fusion conditions were fixed at ore / $KHSO_4$ ratio of 1:3 for 3h. The dissolution efficiencies of metals, plotted on Fig. (10), increased gradually by increasing fusion temp. from 350 to 650 °C where they attained completion for Nb, Ta & REE with Ti 94 % and Zr 20 %. These data indicated that fusion temperature is the most important factor for ore breakdown. However, increasing the fusion temperature to 750 °C has an adverse effect on the dissolution efficiencies of the studied metal values where the dissolution efficiencies decreased to 74.1 % for Nb, 77 % for Ta, 89 % for REE & 74 % for Ti. This decrease may be due to hydrolysis. Zr leaching efficiency was only improved by increasing temp. where it attained 24.5 %.

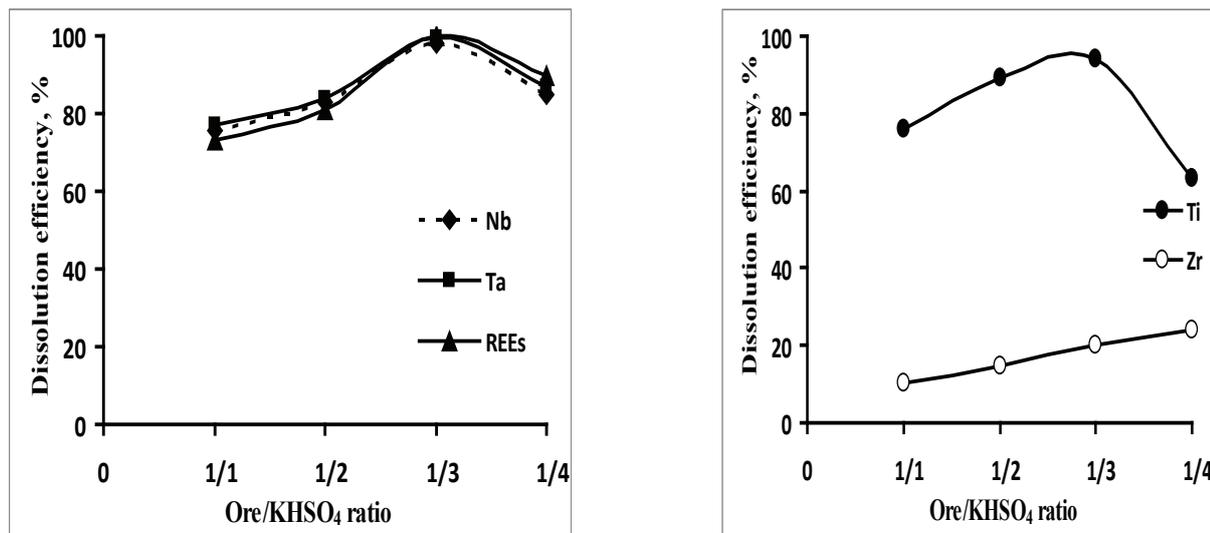


Fig. 9. Effect of Ore/KHSO₄ ratio upon dissolution of the metals of south Gabal El-A'urf ore material.

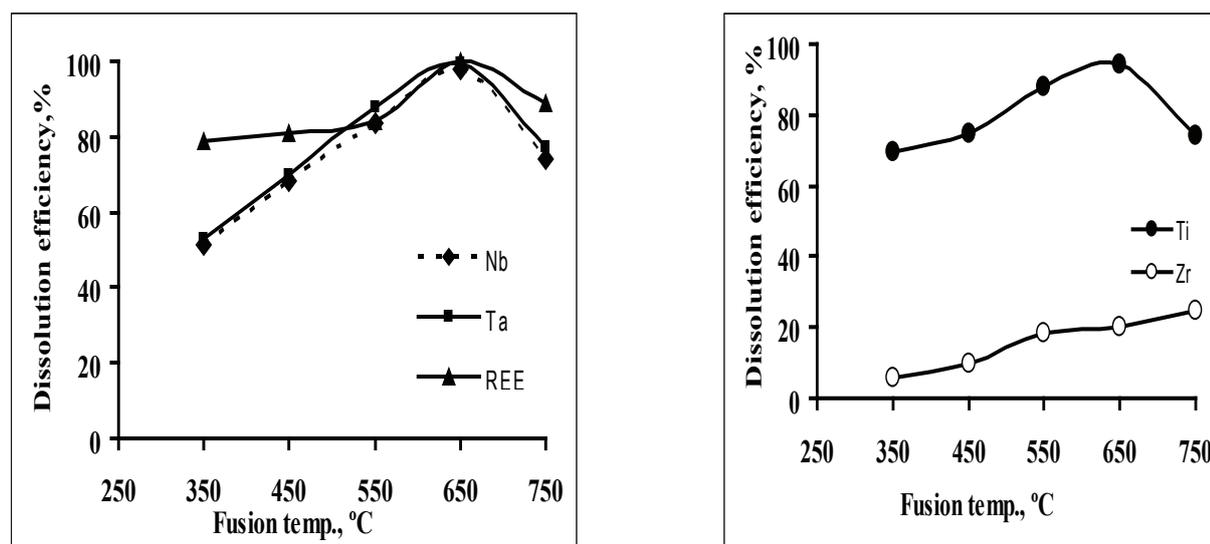


Fig. 10. Effect of fusion temperature upon dissolution of the metals of south Gabal El-A'urf ore material.

iii- Effect of fusion time

A set of experiments was studied ranging from 1 to 4 h. Other fusion conditions were fixed at an ore / KHSO₄ of 1:3 and fusion temperature of 650 °C. The dissolution efficiencies of the studied interesting metal values are plotted in fig. (11). From the results, it is clearly evident that increasing the fusion time from 1 to 3 h. increases the dissolution efficiencies for all metals where it reached 100 % for REE and 99.3 % for Ta, while reached 98 % for Nb, 94 %

for Ti and 20 % for Zr. Further increasing the fusion time to 4 h has adversely affected the dissolution efficiencies of all metals except Zr, most probably due to hydrolysis.

From the above studied fusion factors of south Gabal El-A'urf ore material, it can be concluded that the optimum conditions for dissolving the interesting metal values can be summarized as ore/ KHSO₄ ratio as 1/3 at 650 °C fusion temperature for 3 h. fusion time.

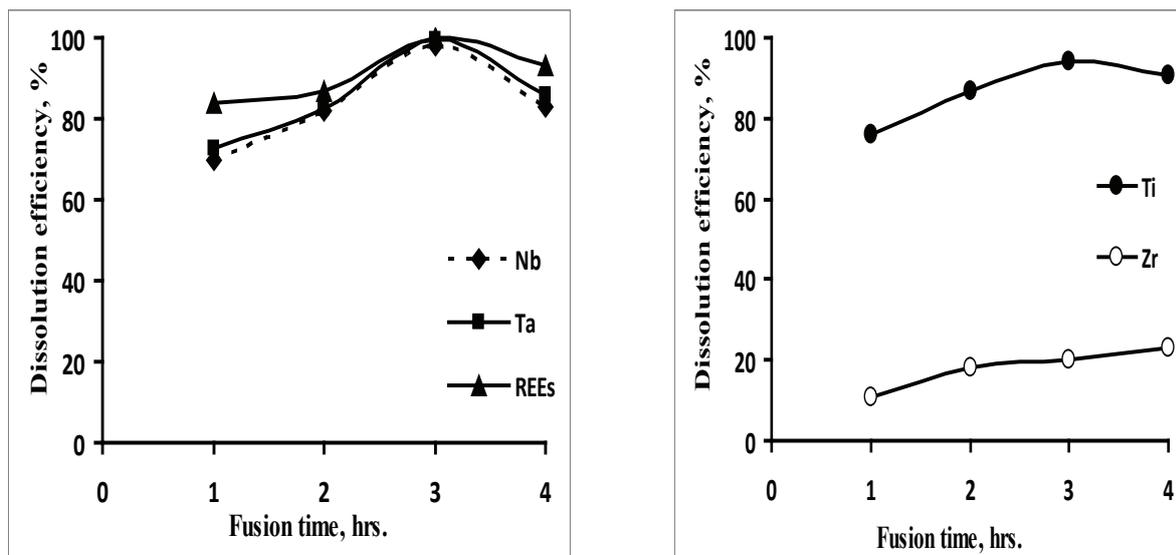


Fig. 10. Effect of fusion temperature upon dissolution of the metals of south Gabal El-A>urf ore material.

Conclusion

Ore characterization of south Gabal El-A>urf proved the presence of several economic minerals. These include tantalum, monazite, bastnaesite, anatase, as well as zircon. Sieve analysis proved that no preferential concentration of any of the interesting metals in certain size fraction since their assay is almost comparable.

Different breakdown techniques have been investigated upon polymineralized ore material of south Gabal El-A>urf. For agitation leaching by sulfuric acid, the optimum conditions were 400g/l acid conc. at 300°C for 3 h using 1/3 S/L ratio. These conditions realized dissolution efficiencies 73% and 78.9% for REE and Ti as well as 10.2% for Zr while keeping Nb and Ta unleached in the residue. On the other hand, using HF/ H₂SO₄ acid mixture increases the dissolution efficiencies up to 95% and 94% for Nb and Ta while sharply decreased REE and Ti to 39.50 and 49.80 as well as 10.8% for Zr. Otherwise, the sulfate leach liquor should be separated before HF addition to keep REE and Ti contents, also to dissolve Nb and Ta in separate HF leach liquor for further recovery steps.

In the meantime, pug leaching by sulfuric acid, achieved low leaching efficiencies for all elements. Otherwise, potassium bisulfate fusion, realized highest dissolution efficiencies for all metals where Nb and Ta attained 98% and 99.3% as well as complete dissolution for REE and 94% for Ti while

Zr not exceed 20% and concentrated in the residue left behind for further treatment. The optimum conditions were 1/3 ore/reagent ratio at 650°C for 3 h. Thus the preferred breakdown technique suitable for this polymineralized ore material is KHSO₄ fusion or alternatively successive agitation leaching using H₂SO₄ acid for REE and Ti then HF acid for Nb, Ta and Zr.

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Received 18 november 2009.